

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:	Haewon Uhm, et al.	Confirmation No. 8739
Filed:	December 11, 2003	Group Art Unit: 1731
Application No.:	10/734,029	Examiner: Dennis R. Cordray
For:	Glass Fiber Sized Web And Process of Making Same	

Mail Stop Appeal Brief  
Commissioner for Patents  
P.O. Box 1450  
Alexandria, VA 22313-1450

RESPONSE TO NON-COMPLAINT APPEAL BRIEF UNDER 37 CFR 41.37

Sir:

In response to the Non-Complaint Appeal Brief dated October 26, 2007, Applicant resubmits an Appeal Brief, which was previously electronically filed on October 9, 2007 for the above-identified application. The Appeal Brief was timely filed with the appropriate fees.

Applicant believes that no fees are due with this filing, however, The Director is hereby authorized to charge any fees or credit any overpayment of same associated with this filing to our Deposit Account No. 03-1250, under Reference No. FDN-2821, Customer No. 43,309.

Respectfully submitted,

Date: November 14, 2007

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Applicant(s)	:	Haewon Uhm, et al.
Serial No	:	10/734,029
Filed	:	December 11, 2003
For	:	GLASS FIBER SIZED WEB AND PROCESS OF MAKING SAME
Examiner	:	Dennis R. Cordray
Art Unit	:	1731
Docket	:	FDN-2821
Dated	:	November 14, 2007

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**APPEAL BRIEF**

This appeal brief is in response to the final Office Action dated January 8, 2007, received in connection with the above-captioned application. Appellants respectfully request reconsideration and reversal of the rejection of that Office Action for the reasons stated below.

TABLE OF CONTENTS

<u>Heading</u>	<u>Page</u>
(i) Real Party In Interest	3
(ii) Related Appeals And Interferences	4
(iii) Status of Claims	5
(iv) Status of Amendments	6
(v) Summary of Claimed Subject Matter	7
(vi) Grounds of Rejection To Be Reviewed on Appeal	9
(vii) Argument	10
(viii) Claims Appendix	15
(ix) Evidence Appendix	19
(x) Related Proceedings Appendix	20

(i) REAL PARTY IN INTEREST

Building Materials Investment Corporation ("BMIC") is the real party in interest, appellants having assigned to BMIC the entire right, title, and interest in and to, *inter alia*, the present application.

(ii) RELATED APPEALS AND INTERFERENCES

Appellants, appellants' assignee, and the undersigned are aware of no related appeals or interferences that may be related to, directly affect or be directly affected by, or have a bearing on the Board's decision in the pending appeal.

(iii) STATUS OF CLAIMS

The pending claims are 1-6 and 8-18. No claim of this application has been allowed. Claim 7 has been cancelled. Claims 1-6 and 8-18 stand rejected; the rejection of these pending claims is appealed herein. Appendix A includes a copy of the appealed claims.

(iv) STATUS OF AMENDMENTS

A response to the Final Office Action was filed but no amendments to the claims were made pursuant to the Final Office Action. All amendments have been entered.

(v) SUMMARY OF CLAIMED SUBJECT MATTER

The claims on appeal relate to a glass fiber web and a wet lay process of making the glass fiber web. The glass fibers of the web include glass fibers sized with a sizing composition which includes a partially amidated polyalkylene imine cationic lubricant randomly dispersed in a cured thermosetting resin. The wet lay process includes the steps of sizing the glass fibers followed by separating such fibers by immersing the glass fibers in an aqueous dispersant medium to form an aqueous dispersion which is agitated. The separated sized glass fibers are dried. The dried, sized glass fibers are then bound with the thermosetting resin binder. The curing of the binder produces the product glass fiber web.

1. A wet lay process for preparing a glass fiber mat comprising the steps of:

(a) sizing glass fibers with a sizing composition which includes a partially amidated polyalkylene imine cationic lubricant {page 3, lines 25-29};

(b) separating said sized glass fibers by immersing said sized glass fibers in an aqueous dispersant medium that includes an emulsifier, whereby a slurry is formed {page 6, lines 10-14};

(c) agitating said slurry causing said emulsifier to generate entrained air, said agitating causing the separation of the glass fibers into individual strands {page 6, lines 12-16};

(d) collecting the individual sized glass fibers on an endless moving conveyor {page 6, lines 18-20};



(e) drying said individual sized glass fibers as the individual sized glass fibers move on the endless moving conveyer {page 6, lines 20-23};

(f) contacting said dried, sized glass fibers with a thermosetting binding resin {page 6, line 25 – page 7, line 15}; and

(g) curing said thermosetting resin whereby a glass fiber mat is formed {page 7, lines 17-20}.

11. A glass fiber web comprising glass fibers sized with a sizing composition which includes a partially amidated polyalkylene imine cationic lubricant {page 3, lines 25-29}, where the glass fibers are added to an aqueous dispersant medium having an emulsifier to generate entrained air to separate the glass fibers into individual glass strands {page 6, lines 10-16}, and further collecting the individual glass fibers on an endless moving conveyer {page 6, lines 18-20} and drying the individual sized glass fibers as they move on the endless moving conveyer during a manufacturing process {page 6, lines 20-23}.

(vi) GROUND OF REJECTION TO BE REVIEWED ON APPEAL

Whether claims 1-6 and 8-18 are patentable under 35 U.S.C. §103(a) over U.S. Pat. No. 5,518,586 to Mirous (hereinafter “Mirous”)<sup>1</sup> in view of U.S. Pat. No. 6,228,281 to Sage (hereinafter “Sage”)<sup>2</sup> and further in view of U.S. Pat. No. 6,432,482 to Jaffee et al. (hereinafter “Jaffee”)<sup>3</sup>.

No other rejections are pending.

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<sup>1</sup> Mirous is attached in the evidence appendix as **Exhibit A**.

<sup>2</sup> Sage is attached in the evidence appendix as **Exhibit B**.

<sup>3</sup> Jaffee is attached in the evidence appendix as **Exhibit C**.

(vii) ARGUMENT

Appellants respectfully request reversal of the rejections of the final Office Action, submitting that the present invention is not unpatentable over Mirous in view of Sage and further in view of Jaffee.

**Claims 1-6 and 8-18 Rejected Under 35 U.S.C. 103(a)**

Responding to the Examiner's rejection of claims 1-6 and 8-18 under 35 U.S.C. 103(a) as being unpatentable over Mirous in view of Sage and further in view of Jaffe, it is submitted that the cited references, individually or in combination, do not teach or suggest the novel elements of independent claims 1 and 11 found in the present invention.

The Examiner asserts that Mirous generally teaches all the steps of claim 1 of the instant invention. The Examiner admits that Mirous does not disclose the composition or properties of the partially amidated polyalkylene imine cationic lubricant, and further, that Mirous does not disclose that the sized fibers have a loss on ignition (LOI) between 0.01% and about 0.75%. However, the Examiner states that Sage discloses treating glass fibers with a sizing composition comprising a cationic lubricant that can be a partially amidated polyalkylene imine. The Examiner also asserts that the "sized fibers disclosed by Sage would inherently have the claimed LOI because, where the claimed and prior art apparatus or product are identical or substantially identical in structure or composition, a prima facie case of either anticipation or obviousness has been established." (Final Office Action, Pages 6, 8).

The Examiner concludes that the art of Mirous, Sage, Jaffee and the instant invention are analogous as they pertain to making nonwoven glass fiber mats. Therefore, the Examiner asserts that it would have been obvious to one of ordinary skill in the art at the time of the invention to use the claimed sizing composition in the mat of Mirous in view of Sage to reduce the breakage of fibers and creation of fuzz on the fiber surface.

However, Sage does not teach fibers for a glass mat. Sage is directed to a sizing composition for coating glass and carbon fibers for use in pultrusion or filament winding operations to reinforce polymeric materials, or used in a knitting or weaving process to produce reinforced fabric (*see* Sage, Col. 1, lines 7-12, Industrial Applicability of the Invention). Sage teaches glass fiber reinforced polymer matrices with applications in plastics such as ladder rails, sucker rods, antennae, railings, conduits, I-beams, H-beams and channel angles, solar collectors, skylights, artificial light fixture covers, patio covers, highway signs, markings and pigmented reinforced sheet molding compound (SMC) applications, such as satellite dishes, showers, bath tubs, automotive body panels, valve covers, spoilers and bumpers (*see* Col. 6, lines 54-64).

On the other hand, the present invention is directed to a wet lay process for preparing a glass fiber mat and a glass fiber web (independent claims 1 and 11, respectively). Therefore, Applicant respectfully submits that it would not be obvious to combine the reference of Sage, which is directed to glass and carbon fibers in the plastics industry, with the reference of Mirous, which is directed to a method of making a glass mat.

Further, the use of a partially amidated polyalkylene imine cationic lubricant (which is not taught by Mirous or Jaffee, as admitted by the Examiner) in preparing a glass fiber mat provides for sufficient strength of the glass fibers. As shown in the specification of the present invention, the use of the partially amidated polyalkylene imine cationic lubricant provides for sufficient strength of the glass fibers so that individual glass fibers are not lost, due to drop off, between the drying and binding steps in a wet lay process of making a glass fiber mat. As shown in Examples 1-6 in Table 1 of the specification, the results make it apparent that wet glass fibers, utilizing prior art sizing compositions, have to be stored up to 3 weeks in order to dry sufficiently to gain the requisite wet strength to successfully be processed. The sizing composition of the present invention eliminates this delay by increasing the wet strength of fully moisturized sized glass fibers such that no delay, occasioned by drying, is required before converting the glass fibers into glass fiber mats.

Further, independent claim 1, a method claim, recites that when the glass fibers are separated by immersing the glass fibers in an aqueous dispersant medium, that aqueous dispersant medium includes an emulsifier, and that when the slurry formed is agitated, the emulsifier generates entrained air and the strands are separated by agitating the slurry formed by the aqueous dispersant medium and the emulsifier. Independent claim 11, an apparatus claim, similarly recites a glass fiber web that includes a partially amidated polyalkylene imine cationic lubricant, where the glass fibers are added to an aqueous dispersant medium having an emulsifier to generate entrained air to separate the glass fibers into individual glass strands.

Mirous is directed to the modification of a urea-formaldehyde resin with a water insoluble anionic phosphate ester as a binder for glass mat obtained from a cationic hydroxyethyl cellulose-containing white water system. According to Mirous in Col. 4, lines 1-3, “[T]he amount of hydroxyethyl cellulose used should be effective to provide the viscosity needed to suspend the glass particles in the white water.”

Unlike Mirous though, the instant invention does not utilize a water insoluble anionic binder (i.e., anionic phosphate ester) in a white water system. While claims 1 and 11 recite agitating a slurry having an emulsifier therein to generate entrained air and cause the separation of glass fibers into individual strands, claims 1 and 11 do not recite, nor require the use of an anionic binder. In fact, as recited on page 6, lines 22-24 of the instant application, it is the thermosetting resin that acts as the binder. According to Mirous, the addition of an anionic phosphate ester to the urea-formaldehyde resin acts to negate the cationic charge of hydroxyethyl cellulose that come in contact with the resin on the glass fibers. Unlike Mirous, the process for preparing a glass fiber mat and glass fiber web as recited in claims 1 and 11 does not utilize a cationic hydroxyethyl cellulose dispersant and thus does not require negation of the cationic charge with an anionic binder.

As such, an element of the present invention as recited in claims 1 and 11 of the present application is not found in Mirous. Combining Mirous with Sage does not cure this defect since Sage teaches the use of a combination of cationic lubricants and nonionic lubricants in low concentrations for achieving increased resistance to fuzz which

develops on broken ends of the glass fibers. Jaffee is not cited for teaching the elements noted above.

The elements of the present invention as recited in claims 1 and 11 of the present application are not taught or suggested by the references of Mirous, Sage and Jaffee, individually or in combination.

It has been held by the Courts that to establish prima facie obviousness of a claimed invention, all the claim limitations must be taught or suggested by the prior art. In re Royka, 490 F.2d 981, 180 U.S.P.Q. 580 (CCPA 1974). The cited references of Mirous, Sage and Jaffee, individually or in combination, fail to teach the claimed limitations of independent claims 1 and 11. Since dependent claims 2-6, 8-10 and 12-18 recite additional unique elements and/or limitations, these claims remain patentable.

For all the above reasons, Appellants respectfully submit that the present claims are not unpatentable over Mirous in view of Sage and further in view of Jaffee.

(viii) CLAIMS APPENDIX

1. A wet lay process for preparing a glass fiber mat comprising the steps of:

(a) sizing glass fibers with a sizing composition which includes a partially amidated polyalkylene imine cationic lubricant;

(b) separating said sized glass fibers by immersing said sized glass fibers in an aqueous dispersant medium that includes an emulsifier, whereby a slurry is formed;

(c) agitating said slurry causing said emulsifier to generate entrained air, said agitating causing the separation of the glass fibers into individual strands;

(d) collecting the individual sized glass fibers on an endless moving conveyer;

(e) drying said individual sized glass fibers as the individual sized glass fibers move on the endless moving conveyer;

(f) contacting said dried, sized glass fibers with a thermosetting binding resin; and

(g) curing said thermosetting resin whereby a glass fiber mat is formed.

2. A process in accordance with Claim 1 wherein said partially amidated polyalkylene imine cationic lubricant comprises between about 0.005% and about 0.20% by weight, said percentages being by weight, based on the total weight of the sizing composition.

3. A process in accordance with Claim 1 wherein said partially amidated polyalkylene imine has a residual amine value of from about 200 to about 800 and is the reaction product of fatty acids containing between about 2 and about 18 carbon atoms and a polyethylene imine having a molecular weight of from about 800 to about 50,000.



4. A process in accordance with Claim 1 wherein said sized glass fibers have a loss on ignition in the range of between about 0.01% and about 0.75%.

5. A process in accordance with Claim 4 wherein said sized glass fibers have a loss on ignition in the range of between about 0.05% and about 0.5%.

6. A process in accordance with Claim 1 wherein said step (b) of separating said sized glass fibers occurs in the presence of an emulsifier to generate entrained air.

8. A process in accordance with Claim 1 wherein said binding step (f) occurs on an endless moving conveyer disposed adjacent to said endless moving conveyer employed in drying said dried sized glass fibers.

9. A process in accordance with Claim 8 wherein said thermosetting binding resin is urea formaldehyde:

10. A process in accordance with Claim 1 wherein said curing step (g) occurs by heating said product of step (f) at a temperature of at least about 175°C.

11. A glass fiber web comprising glass fibers sized with a sizing composition which includes a partially amidated polyalkylene imine cationic lubricant, where the glass fibers are added to an aqueous dispersant medium having an emulsifier to generate entrained air

to separate the glass fibers into individual glass strands, and further collecting the individual glass fibers on an endless moving conveyer and drying the individual sized glass fibers as they move on the endless moving conveyer during a manufacturing process.

12. A web in accordance with Claim 11 wherein said sized glass fibers are dispersed in a cured thermosetting resin.

13. A web in accordance with Claim 12 wherein said partially amidated polyalkylene imine cationic lubricant comprises between about 0.005% and about 0.02%, said percentages being by weight, based on the total weight of the sizing composition.

14. A web in accordance with Claim 13 wherein said sized glass fibers have a loss on ignition in the range of between about 0.01% and about 0.75%.

15. A web in accordance with Claim 14 wherein said sized glass fibers have a loss on ignition in the range of between about 0.05% and about 0.5%.

16. A web in accordance with Claim 15 wherein said sized glass fibers have a loss on ignition in the range of between about 0.1% and about 0.2%.

17. A web in accordance with Claim 14 wherein said partially amidated polyalkylene imine has a residual amine value of from about 200 to about 800 and is the reaction product of fatty acids containing between about 2 and about 8 carbon atoms and a polyethylene imine having a molecular weight of from about 800 to about 50,000.

18. A web in accordance with Claim 11 wherein said cured thermosetting resin is cured urea formaldehyde.

(ix) EVIDENCE APPENDIX

Exhibit A - Mirous (U.S. Pat. No. 5,518,586), referred to on pages 4-6 of the Final Office Action.

Exhibit B - Sage (U.S. Pat. No. 6,228,281), referred to on pages 6-7 of the Final Office Action.

Exhibit C - Jaffee (U.S. Pat. No. 6,432,482), referred to on pages 2-3 and 7-8 of the Final Office Action.

Exhibit A



US005518586A

**United States Patent** [19][11] **Patent Number:** **5,518,586****Mirous**[45] **Date of Patent:** **May 21, 1996**[54] **METHOD OF MAKING A HIGH TEAR  
STRENGTH GLASS MAT**[75] **Inventor:** **George E. Mirous, Tacoma, Wash.**[73] **Assignee:** **Georgia-Pacific Resins, Inc., Atlanta,  
Ga.**[21] **Appl. No.:** **450,151**[22] **Filed:** **May 26, 1995****Related U.S. Application Data**[62] **Division of Ser. No. 123,094, Sep. 20, 1993, Pat. No.  
5,445,878.**[51] **Int. Cl.<sup>5</sup>** ..... **D04H 1/64**[52] **U.S. Cl.** ..... **162/156; 162/158; 162/167;  
162/186; 156/62.2**[58] **Field of Search** ..... **162/156, 167,  
162/158, 166, 186, 184; 156/62.2; 264/109**[56] **References Cited****U.S. PATENT DOCUMENTS**2,906,660 9/1959 Hungerford et al. .  
3,012,929 12/1961 Jackson .  
3,050,427 8/1962 Slayter et al. .  
3,103,461 9/1963 Smith et al. .3,228,825 1/1966 Waggoner .  
3,760,438 9/1973 Pitt .  
3,766,003 10/1973 Schuller et al. .  
3,838,995 10/1974 Smith .  
3,905,067 9/1975 Keib et al. .  
4,178,203 12/1979 Chakrabarti .  
4,210,462 7/1980 McCombs .  
4,210,562 7/1980 McCombs .  
4,258,098 3/1981 Bowdler et al. .  
4,430,158 2/1984 Jackey et al. .  
4,457,785 7/1984 Hsu et al. .  
4,536,446 8/1985 Hsu et al. .  
4,681,658 7/1987 Hsu et al. .  
4,683,165 7/1987 Linderman et al. .  
4,917,764 4/1990 Lalwani et al. .  
5,190,997 3/1993 Lindemann et al. .  
5,219,656 6/1993 Klett et al. .**Primary Examiner**—Michael W. Ball  
**Assistant Examiner**—Sam Chuan Yao  
**Attorney, Agent, or Firm**—Banner & Allegretti, Ltd.[57] **ABSTRACT**

A urea-formaldehyde resin modified with a water-insoluble anionic phosphate ester is used as binder in the preparation of glass fiber mats using a hydroxyethyl cellulose white water system. High tear strength glass fiber mats can be produced in a hydroxyethyl cellulose white water system using such a binder.

**2 Claims, No Drawings**

# METHOD OF MAKING A HIGH TEAR STRENGTH GLASS MAT

This application is a division of application Ser. No. 08/123,094, filed Sep. 20, 1993, now U.S. Pat. No. 5,445, 878.

## BACKGROUND OF THE INVENTION

### 1. Field of the Invention

The invention relates to a modified urea-formaldehyde resin, to glass fiber mats using the modified urea-formaldehyde resin as binder, and a process of preparing the mats. In particular, the invention relates to a urea-formaldehyde resin modified with a water-insoluble anionic phosphate ester which is useful in the preparation of glass fiber mats formed using a hydroxyethyl cellulose-containing "white water" glass slurry. The glass fiber mats of the invention exhibit high tear strength, a property which is desirable for use in roofing products, such as asphalt shingles.

### 2. Background of the Invention

Glass fiber mats are finding increasing application in the building materials industry, as for example, in asphalt roofing shingles, replacing similar sheets traditionally made of wood or cellulose fibers.

Glass fiber mats usually are made commercially by a wet-laid process, which is carried out on modified paper or asbestos making machinery. Descriptions of the wet-laid process may be found in a number of U.S. patents, including U.S. Pat. Nos. 2,906,660, 3,012,929, 3,050,427, 3,103,461, 3,228,825, 3,760,458, 3,766,003, 3,838,995 and 3,905,067. In general, the known wet-laid process for making glass fiber mats comprises first forming an aqueous slurry of short-length glass fibers (referred to in the art as "white water") under agitation in a mixing tank, then feeding the slurry through a moving screen on which the fibers enmesh themselves into a fleshly prepared wet glass fiber mat, while water is separated therefrom.

Unlike natural fibers such as cellulose or asbestos, glass fibers do not disperse well in water. In an attempt to overcome this problem, it has been the practice in the industry to provide suspending aids for the glass fibers. Such suspending aids usually are materials which increase the viscosity of the medium so that the fibers can suspend themselves in the medium. Suitable dispersants conventionally employed in the art include polyacrylamide, hydroxyethyl cellulose, ethoxylated amines and amine oxides.

Other additives such as surfactants, lubricants and defoamers have conventionally been added to the white water. Such agents, for example, aid in the wettability and dispersion of the glass fibers and contribute to the strength of the wet glass fiber mat. U.S. Pat. No. 4,178,203 is directed to a method for improving the wet tensile strength of freshly prepared glass fiber mats so that they may be conveniently handled and transferred for further processing (e.g., applying binders and drying) to form the finished glass fiber mat product. In the disclosed process, anionic surfactants are added to the white water glass slurry.

In the manufacture of glass mat, a high degree of flexibility and tear strength is desired in addition to the primary dry tensile and hot wet tensile properties. A binder material

is therefore used to hold the glass fiber mat together. The binder material is impregnated directly into the fibrous mat and set or cured to provide the desired integrity. The most widely used binder is urea-formaldehyde resin because it is inexpensive.

While urea-formaldehyde resins are commonly used to bond the glass fibers together to provide the strength properties of the glass mat, some urea-formaldehyde resin binders are too brittle to form glass mats useful in roofing shingles. Typically, the tensile strengths of mats bound with urea-formaldehyde deteriorate appreciably when the mats are subjected to wet conditions, such as the conditions normally encountered by roofing products. Tear strengths higher than those typically provided by urea-formaldehyde resins have been obtained by modifying the resin with cross-linkers and various catalyst systems or by fortifying the resin with a large amount of latex polymer, usually a polyvinyl acetate, vinyl acrylic or styrene-butadiene. Latex provides increased hot wet tensile strength and tear strength. The use of styrene-butadiene modified urea-formaldehyde resins as a binder for glass fiber mats is disclosed, for example, in U.S. Pat. Nos. 4,258,098 and 4,917,764.

U.S. Pat. No. 4,430,158 is directed to an improved binder composition for glass mats. The binder composition consists essentially of a urea-formaldehyde resin and a highly water soluble anionic surfactant that wets the surfaces of the glass fibers. Suitable surfactants have hydrophobic segments containing from 8 to 30 carbon atoms and anionic segments. Suitable anionic moieties include carboxy, sulfate ester, phosphate ester, sulfonic acid, and phosphoric acid groups. The surfactant also may contain a polyalkyleneoxy chain having up to 10 alkyleneoxy units. Glass mats produced from an amine oxide white water system and bound with the surfactant-containing resin, are described as retaining up to 79 percent of their dry tensile strength when subjected to severe wet conditions. No increase in tear strength is obtained by use of the urea-formaldehyde surfactant-containing resin. Cationic surfactants, non-ionic surfactants, and anionic surfactants which do not possess the required water solubility and ability to wet the sized glass fibers, are said to provide unsuitable mats which can retain a much smaller fraction of their dry tensile strength.

When the glass fibers are dispersed in white water containing a polyacrylamide viscosity modifier, high tear mat strengths have been achieved with latex fortification of urea-formaldehyde resins. However, when a hydroxyethyl cellulose viscosity modifier is used in the white water, the desired high tear strength properties are not achieved with latex fortification. As such, a need in the art exists for providing a modified urea-formaldehyde resin which can be used in a hydroxyethyl cellulose white water system.

## SUMMARY OF THE INVENTION

The invention is directed to a modified urea-formaldehyde resin. The invention also is directed to a process for preparing glass fiber mats, and to glass fiber mats produced by the method. The mats are useful in, for example, the manufacture of roofing shingles.

This invention is based on the discovery that by adding a water-insoluble anionic phosphate ester to a urea-formal-

hyde resin, high tear strength products can be prepared from mats formed using hydroxyethyl cellulose-containing white water.

In manufacturing glass fiber mats in accordance with the invention, glass fibers are slurried into an aqueous medium containing hydroxyethyl cellulose. This white water, i.e., the hydroxyethyl cellulose-containing slurry of glass fibers in water, then is dewatered on a foraminated surface to form a mat. The modified binder of the invention then is applied to the mat before it passes through a drying oven where the mat is dried and incorporated binder resin is cured. Glass fiber mats produced in accordance with the invention exhibit good dry and hot wet tensile strength and superior high tear strength.

One object of the invention is to provide a binder composition for use in making glass fiber mats comprising a urea-formaldehyde resin and a water-insoluble anionic phosphate ester.

Another object of the invention is to provide glass fiber mats comprising a urea-formaldehyde resin and a water-insoluble anionic phosphate ester.

Yet another object of the invention is to provide glass fiber mats prepared by dispersing glass fibers in an aqueous medium containing hydroxyethyl cellulose to form a slurry, passing the slurry through a mat forming screen to form a wet glass fiber mat, applying a binder comprising a urea-formaldehyde resin and a water-insoluble anionic phosphate ester to said wet glass fiber mat, and curing the binder.

#### DETAILED DESCRIPTION OF THE INVENTION

Urea-formaldehyde resins have been modified with cross-linkers and various catalyst systems or fortified with large amounts of latex to achieve high glass mat tear strengths in mats processed in polyacrylamide-containing white water. However, such modified and fortified resins have no effect in a hydroxyethyl cellulose-containing white water system. It has now been discovered that the modification of urea-formaldehyde resin with a water-insoluble anionic phosphate ester as a binder for glass mat obtained from a hydroxyethyl cellulose-containing white water system not only provides higher tear strength without a loss in dry or hot wet tensile properties, but also does not require latex fortification. This not only eliminates handling and clean up problems associated with latexes, but is also significantly lower in cost.

The process of forming a glass fiber mat in accordance with the invention begins with chopped bundles of glass fibers of suitable length and diameter. While reference is made using chopped bundles of glass fibers, other forms of glass fibers such as continuous strands may also be used. Generally, fibers having a length of about ¼ inch to 3 inches and a diameter of about 3 to 20 microns are used. Each bundle may contain from about 20 to 300, or more, of such fibers.

The glass fiber bundles are added to the dispersant medium to form an aqueous slurry, known in the art as "white water." The white water typically contains about 0.5% glass. The dispersant used in the practice of the invention contains

hydroxyethyl cellulose. The amount of hydroxyethyl cellulose used should be effective to provide the viscosity needed to suspend the glass particles in the white water. The viscosity is generally in the range of 5 to 20 cps, preferably 12 to 14 cps. An amount of from about 0.1 to about 0.5% solid hydroxyethyl cellulose in the water should be sufficient. The fiber/white water mixture generally is at a temperature of 65° to 95° F. to obtain preferred viscosity. The fiber slurry then is agitated to form a workable uniform dispersion of glass fiber having a suitable consistency. The dispersant may contain other conventional additives known in the art. These include surfactants, lubricants, defoamers and the like.

The fiber/white water dispersion then is passed to a mat-forming machine containing a mat forming screen. On mute to the screen, the dispersion usually is diluted with water to a lower fiber concentration. The fibers are collected at the screen in the form of a wet fiber mat and the excess water is removed by gravity or, more preferably, by vacuum in a conventional manner.

The binder composition of the invention then is applied to the gravity- or vacuum-assisted dewatered wet glass mat. Application of the binder composition may be accomplished by any conventional means, such as by soaking the mat in an excess of binder solution, or by coating the mat surface by means of a binder applicator.

The urea-formaldehyde resin used as binder in the invention is a urea-formaldehyde resin modified with an anionic phosphate ester. The anionic phosphate esters useful in the invention are water insoluble. Particularly preferred anionic phosphate esters are unneutralized water insoluble phosphate esters, such as the type exemplified by ZELEC UN® available from Du Pont. ZELEC UN® is an unneutralized, water-insoluble anionic phosphate ester with a high molecular weight  $C_{12}$  to  $C_{18}$  fatty alcohol backbone. Stated another way, ZELEC UN® is an unneutralized water-insoluble, anionic phosphate  $C_3$  of  $C_{18}$  alkyl ester of phosphoric acid and a fatty alcohol. A urea-formaldehyde resin modified with ZELEC UN® has been found to be particularly advantageous in the preparation of glass fiber mats having high tear strength from hydroxyethyl cellulose white water.

Methods of preparing urea-formaldehyde resins which may be used to prepare the binder composition of the invention are known to those skilled in the art. Many urea-formaldehyde resins which may be used in the practice of the invention are commercially available. Urea-formaldehyde resins such as the types sold by Georgia Pacific Corp. for glass mat application and those sold by Borden Chemical Co., may be used. These resins generally are modified with methylol groups which upon curing form methylene or ether linkages. Such methylols may include N,N'-dimethylol, dihydroxymethylolethylene; N,N' bis-(methoxymethyl), N,N'-dimethylolpropylene; 5,5-dimethyl-N,N' dimethylolpropylene; N,N'-dimethylolethylene; and the like.

The binder composition is prepared by rapidly dispersing the anionic phosphate ester into the urea-formaldehyde resin having a pH of 7.5 to 8.5. If needed pH of the resin is adjusted to 7.5 to 8.5 with caustic. The amount of phosphate ester is about 0.1 to about 5.0%, preferably about 0.5% of the binder composition.



Urea-formaldehyde resins useful in the practice of the invention generally contain 45 to 65%, preferably, 50 to 60% non-volatiles, have a viscosity of 50 to 500 cps, preferably 150 to 300 cps, a pH of 7.0 to 9.0, preferably 7.5 to 8.5, a free formaldehyde level of 0.0 to 3.0%, preferably 0.1 to 0.5%, a mole ratio of formaldehyde to urea of 1.1:1 to 3.5:1, preferably 1.8:1 to 2.1:1, and a water dilutability of 1:1 to 100:1, preferably 10:1 to 50:1.

Whereas high tear strength mats can be prepared using latex-fortified binders when the white water additive is polyacrylamide, high strength mats have not heretofore been prepared using hydroxyethyl cellulose. In contrast to the polyacrylamide white water system, which has an anionic charge and has chemical attraction for a weak to strong cationic urea-formaldehyde resin, hydroxyethyl cellulose is a cationic viscosity modifier. While not wishing to be bound to a particular theory, it is believed that the addition of an anionic phosphate ester to the urea-formaldehyde resin acts to negate the cationic charge of hydroxyethyl cellulose that comes in contact with the resin on the glass fibers.

containing 22 to 25% solids was applied on the fiber mat and excess binder removed by vacuum. The mat was then placed in a Werner Mathis oven for 60 seconds at 205° C. to cure the resin.

#### EXAMPLE 2

A commercially available urea-formaldehyde resin (GP 2928) was used as a control resin. This control resin, GP 2928 resin fortified with 23% polyvinyl acetate (PVAc), and resin modified with 0.5% ZELEC UN® (GP 328T67) were used as binder to prepare glass fiber mats as described in Example 1.

Seven 3"×5" cut samples were tested for tensile strength under dry conditions and after soaking in an 85° C. water bath for 10 minutes on an Instron with a crosshead speed of 2 inches and a jaw span of 3 inches. Tear strength was tested on 2.5"×3.0" cut samples using an Elmdorf Tear Machine. The mean values of all tests are shown in Table I.

TABLE I

Resins	Mat. Wt.*	% LOI	Dry Tensile <sup>b</sup>	Hot Wet Tensile <sup>b</sup>	% R	Tear <sup>c</sup>
GP 2928	1.80	24	117	81	69	390
GP 2928 + 23% PVAc	1.75	22	115	75	65	380
GP 328T67 (+ 0.5% ZELEC UN®)	1.75	21	129	78	60	515

\*pounds per hundred square foot

<sup>b</sup>pounds for a 3" wide sheet

<sup>c</sup>grams

Following application of the binder, the glass fiber mat is dewatered under vacuum to remove excess binder solution. The mat then is dried and incorporated binder composition is cured in an oven at elevated temperatures, generally at a temperature of at least about 200° C., for a time sufficient to cure the resin. The amount of time needed to cure the resin is readily determinable by the skilled practitioner. Heat treatment alone is sufficient to effect curing. Alternatively, but less desirably, catalytic curing in the absence of heat may be used, such as is accomplished with an acid catalyst, e.g., ammonium chloride or p-toluene sulfonic acid.

The finished glass mat product generally contains between about 60% and 90% by weight glass fibers and between about 10% and 40% by weight of binder, 15-30% of binder being most preferable.

The following examples are intended to be illustrative only and do not limit the scope of the claimed invention.

#### EXAMPLE 1

Glass fiber mats were prepared by adding 0.5 gms of surfactant (Katapol VP-532), 0.1 gms of defoamer (Nalco 2343) and 6.5 gms of Manville 1" cut glass fibers obtained from Schuller International to 7.5 liters of hydroxyethyl cellulose-containing white water having a viscosity of 12 to 14 cps and mixed for 3 minutes. Excess water was drained and then vacuum dewatered on a foraminated surface to form a wet glass fiber mat. A urea-formaldehyde binder

Dry tensile strength, hot water tensile strength and percent retention (%R) of dry tensile strength under hot wet condition (hot wet/dry) of the urea-formaldehyde resin containing ZELEC UN® compare favorably to those of the control (urea-formaldehyde resin) and the latex fortified urea-formaldehyde resins. In contrast, the ZELEC UN® modified urea-formaldehyde resin produced a glass fiber mat having superior tear strength compared to the control urea-formaldehyde resin and the latex fortified urea-formaldehyde resin.

#### EXAMPLE 3 (COMPARISON)

Glass fiber mats were prepared as described in Example 1 except the hydroxyethyl cellulose white water system was replaced by a polyacrylamide white water system containing 0.02 to 0.1% polyacrylamide and having a viscosity of 4-10 cps, preferably 6 cps. A commercially available latex fortified urea formaldehyde resin (GP 2928 containing 23% PVAc), a commercially available urea-formaldehyde resin modified with a polyamine (GP 2942) and a urea formaldehyde resin containing 0.5% ZELEC UN® (GP 328T67) were used to cure the glass fiber mats as described in Example 2. Dry and hot wet tensile strength and tear strength was determined as described in Example 2. The results are shown in Table II. The values shown in Table II are the ranges of the means of 5 studies, 7 samples per study.

TABLE II

Resins	Mat. Wt.	% LOI	Dry Tensile	Hot Wet Tensile	% R	Tear
GP 2928 23% PVAc	1.60-1.90	18-25	120-140	65-104	50-80	300-350
GP 2942 (+ polyamine modifier)	1.60-1.90	18-25	120-140	65-104	50-80	400-500
GP 328T67 (+0.5% ZELEC UN @)	1.60-1.90	18-25	120-140	65-104	50-80	300-350

## EXAMPLE 4

Glass fiber mats prepared as described in the hydroxyethyl cellulose white water system of Example 1 were cured with the same resins used in Example 3 and tested for dry and hot wet tensile strength and tear strength as described in Example 2. The results (range mean values of 5 studies—7 samples per study) are shown in Table III.

TABLE III

Resins	Mat. Wt.	% LOI	Dry Tensile	Hot Wet Tensile	% R	Tear
GP 2928 + 23% PVAc	1.60-1.80	18-25	100-110	53-84	50-80	360-400
GP 2942 (+ polyamine modifier)	1.60-1.80	18-25	110-120	59-92	50-80	380-450
GP 328T67 (+ 0.5% ZELEC UN @)	1.60-1.80	19-25	120-130	63-100	50-90	500-600

The use of a phosphate ester modified-resin provided higher tear strength to glass mats prepared using a hydroxyethyl cellulose white water system. The high tear strength obtained in Examples 2 and 4 for glass mats prepared using

and hot wet tensile strength and tear strength as described in Example 2. The mean values are shown in Table IV.

TABLE IV

Resins	Dry Tensile	Hot Wet Tensile	% Retention	Tear Strength	Mat Wt.	% LOI
GP 2928 + 25% PVAc	139	96	70	350	1.80	29
GP 328T67 (+ ZELEC UN @)	140	89	63	490	1.80	28
GP 2928 (+ ZELEC TY @)	141	104	74	300	1.90	28

the hydroxyethyl cellulose white water system could not be obtained using the polyacrylamide white water system of Example 3.

## EXAMPLE 5

Glass fiber mats prepared as described in the hydroxyethyl cellulose white water system of Example 1 were cured with a commercially available latex fortified urea-formaldehyde resin (GP 2928 containing 25% PVAc), a urea-formaldehyde resin containing 0.5% ZELEC UN@ (GP 328T67) or a urea-formaldehyde resin containing 0.5% ZELEC TY@. ZELEC TY@ is a neutralized, water-soluble anionic phosphate ester with a lower molecular weight fatty alcohol backbone. The glass fiber mats were tested for dry

As can be seen in Examples 2 and 4, resins modified with water-insoluble anionic phosphate esters, such as ZELEC UN@, provide significantly higher tear strength in glass mat than latex fortified urea-formaldehyde resins when the glass mat is formed using a hydroxyethyl cellulose white water system. Although use of the water-soluble ZELEC TY@ modified binder gave dry and hot wet tensile strength equal to the latex fortified binder, the ZELEC TY@ modified binder did not improve the tear strength properties compared to the latex fortified binder, as did the water-insoluble ZELEC UN@ modified binder.

I claim:

1. A method of making a glass fiber mat comprising: dispersing glass fibers in an aqueous medium containing hydroxyethyl cellulose to form a slurry,

passing the slurry through a mat forming screen to form a wet glass fiber mat,

applying a binder comprising a urea-formaldehyde resin and a water-insoluble, unneutralized anionic phosphate ester, a  $C_8$  to  $C_{16}$  fatty alcohol to said wet glass fiber mat, and

curing the binder.

2. The method of claim 1 wherein the anionic phosphate ester is present in an amount of from about 0.1% to about 5.0% based on the weight of the binder.

\* \* \* \* \*

Exhibit B



US006228281B1

**(12) United States Patent**  
**Sage****(10) Patent No.: US 6,228,281 B1**  
**(45) Date of Patent: May 8, 2001**

- (54) **SIZING FOR GLASS FIBERS HAVING LOW NONIONIC AND CATIONIC LUBRICANT CONTENT**
- (75) Inventor: Donald B. Sage, Amarillo, TX (US)
- (73) Assignee: Owens Corning Fiberglas Technology, Summit, IL (US)

(\*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

- (21) Appl. No.: 09/182,462
- (22) Filed: Oct. 30, 1998

- (51) Int. Cl.<sup>7</sup> ..... C03C 17/28; C03C 17/30; D06M 13/00; D06M 15/643
- (52) U.S. Cl. .... 252/8.83; 252/8.84; 65/443; 65/444; 65/448; 8/115.6; 524/186; 524/261; 525/29; 525/101
- (58) Field of Search ..... 252/8.83, 8.84; 65/443, 444, 448; 8/115.6; 524/186, 261; 525/29, 101

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**(57) ABSTRACT**

A sizing composition for coating glass and carbon fibers. The composition comprises low concentrations of a cationic and nonionic lubricant, a film-forming polymer, and preferably a coupling agent and a hydrolyzing agent. Use of the sizing composition reduces fuzz development, increases wettability, and improves roving package stability.

**14 Claims, No Drawings**

1

# **SIZING FOR GLASS FIBERS HAVING LOW NONIONIC AND CATIONIC LUBRICANT CONTENT**

## **TECHNICAL FIELD AND INDUSTRIAL APPLICABILITY OF THE INVENTION**

The present invention relates to a sizing composition for coating glass or other fibers derived from amorphous material. These fibers may be used, for example, in pultrusion or filament winding operations to reinforce polymeric materials, or are used in a knitting or weaving process to produce reinforced fabric. More specifically, the invention is a composition having low levels of nonionic and cationic lubricant additives that is used to effectively coat glass, carbon or aramid fibers. This coating endows the fibers with enhanced properties such as reduced fuzz development and improved roving package stability.

## **BACKGROUND OF THE INVENTION**

The reinforced plastic industry has historically used glass fibers in the form of continuous or chopped fibers, strands and rovings to reinforce polymer matrices used in making a wide range of products. In particular, glass fibers, as well as woven and non-woven fabrics, meshes and scrims have been added to thermosetting polymer matrices for use in pultrusion, filament-winding, spray-up, sheet molding and bulk molding operations.

In the pultrusion process, for example, a reinforced composite is formed when a thermosetting polymer or a hot thermoplastic polymer is forced between the fibers of a glass roving as it is pulled through a coating apparatus, profiling and alignment dies. In this manner, the fibers are impregnated with the polymer resin, and the resin and fibers are shaped into the form of the composite. In turn, these impregnated composites are cured by heating continuously. The glass fibers, strands and rovings used in the pultrusion operation are made from molten fiberizable material that is introduced into a bushing or like device. The bushing is equipped with small apertures to allow passage of thin streams of the molten material. As the molten material emerges from the bushing apertures, each stream is attenuated and pulled downward to form a long, continuous fiber. The continuously forming fibers may be gathered into strands for winding. Winding is accomplished by attaching the strands to a mechanism such as a winder or pull wheel, and then winding the fibers onto spools or reels. The rate at which the winder pulls the fiber determines its width, with more rapid attenuation creating thinner fibers of smaller diameter, and a slower speed generating thicker fibers. The rate of attenuation also affects the movement of the filaments through the fiber-forming process, and therefore also affects the amount of any coating material deposited on the surface of the moving fibers. The forming packages or dolls formed by the above-described winding operation are then ready for use in composite-making operations such as pultrusion or filament winding.

Several difficulties have been associated with the use of continuous fibers and the rovings made from these fibers. A major problem with the use of wound rovings is the breakage of the individual fibers during winding, unwinding or handling of the strands. Inter-filament abrasion of the fibers causes them to break, and as a result loose ends are separated from the fiber strands. These loose, broken ends form a roughened layer or fuzz on the surface of the fibers. Fuzz may also develop when fibers break during the weaving process. This fuzz is undesirable because it affects the

2

appearance of the woven product. Breakage of the fibers also results in build-up of fuzz on the contact points and other surfaces of the processing machinery. This fuzz buildup in turn is exacerbated by static electricity. Also, the fuzz often becomes airborne, and thus becomes a source of skin and respiratory irritation to some workers handling the fiber strands. The fuzz may also collect to form tufts or balls of broken fibers, which then jam the processing equipment or fall into the resin baths used for dipping the fiber strands.

It has long been recognized that, in order to reduce fuzz, it is advantageous to provide a light coating known as a size or size coating onto the surface of the glass or carbon fibers after they have been attenuated from the bushing. The size coating is particularly desirable when the fibers are to be used as reinforcing elements in resinous articles. The size coating reduces fuzz and improves processing properties of the fibers such as fiber bundle cohesion, spreadability, fiber smoothness and softness, abrasion resistance and ease in unwinding the fiber bundles. The compositions are further used to make the glass fibers compatible with the polymer matrices to which they are added as a reinforcing component.

The size may be applied to the fibers in an on-line operation immediately after they are formed, or they may be applied off-line to unwound fiber strands that were previously formed and packaged. Preferably, the fibers are wet with the sizing composition as soon as they are formed from the bushing. The application of the composition at this early stage helps to protect the fibers from damage during handling. The sizing is applied by conventional means, then dried onto the surface of the fibers. Heat may be used to dry and/or cure the coating.

Generally, sizing agents can be divided into two types, the solvent type and the emulsion type. Non-aqueous solvent type size compositions include a low-boiling organic solvent combined with the ingredients to form a solution that is applied to the fibers. In emulsion sizing agents, the resin and other ingredients are dispersed in water to form an emulsion, which is then applied to the filaments. The filaments are dried to provide a uniform coating of the sizing agent.

Chemical sizing compositions have traditionally been aqueous solutions, foams or gel compositions containing a film-forming polymer, coupling or keying agent, and lubricant. Typically, the focus in the art has been concentrated on developing sizing compositions that either maximize the amount of coating on the fibers to reduce fuzz; or on eliminating undesirable features of coated roving, such as tackiness or flaking. As a result, the sizing compositions that are usually used in the art to reduce fuzz formation include high levels of lubricants or other ingredients. Coatings as exemplified by U.S. Pat. Nos. 5,393,335, 5,605,757, 5,665, 470, 5,334,639, 5,286,562, 4,795,678, 4,762,751, relate to sizing compositions for treating glass fibers having one or more ingredients such as lubricants, emulsifiers, humectants, coupling agents or natural or synthetic polymers. However, the high levels of lubricants traditionally used in these size coatings routinely result in over-lubrication of the strands or rovings. When these over-lubricated rovings are wound, the forming packages become unstable because of slippage of the strands. The rovings may also be squeezed together during the packaging, thus changing the height of the doll. As a result, the formed packages are not of uniform height, and they cannot be stacked or palletized for efficient storage. Rather, stacking pallets with unevenly sized packages may cause the pallets to collapse, thereby jeopardizing worker safety. The lack of uniform size may also result in the packages not being able to fit onto apparatus used to mold

or form composites. Use of higher amounts of lubricants has also increased the costs associated with the sizing operation.

Another problem related to the use of sizing compositions is incompatibility between the sizing composition and the polymer matrix used to form the composites. The art has attempted in several ways to solve the problem of incompatibility between the fibers and the polymer composite material into which they are implanted, including the development of compositions containing curing or coupling agents. However, there remains a recognized need for a coupling agent that facilitates intimate bonding between the glass fibers and the polymer matrix.

There exists then a need for a sizing composition that will provide an effective coating to reduce fuzz, while improving rather than decreasing the stability of the roving package. Further, a sizing composition that yields an effective coating, but at the same time requires a low concentration of ingredients is desirable because waste is minimized.

#### SUMMARY OF THE INVENTION

It is therefore an object of this invention to provide a composition which, when used to coat reinforcing fiber rovings, reduces fuzz development and at the same improves the stability of the forming packages. The term stability as it is used here is intended to mean a condition in which substantially no slippage of the sized rovings occurs when they are wound onto the reels; and in which the forming packages are of a consistent and uniform size that permits them to be stably stacked onto pallets, or which makes the packages compatible with apparatus designed for composite molding. It is also an object of this invention to produce a sizing composition that is cost-effective to make and use.

More specifically, it is an object of this invention to provide a sizing composition having low levels of cationic and nonionic lubricants, wherein the combination of these lubricants at the prescribed levels is compatible with polymers used for coating the fibers and for making the composite articles. The composition of this invention is suitable for coating reinforcing fibers selected from the group consisting of reinforcing glass, carbon or aramid fibers.

It has now surprisingly been found that when low concentrations of an alkoxylated polyalkylene glycol monoester lubricant and a partially amidated polyalkylene imine cationic lubricant are combined with a film-forming polymer, such that the lubricant concentrations are lower than those previously contemplated by the prior art, the resulting sizing composition is effective in reducing fuzz and in stabilizing the fiber roving package. The concentration of the glycol monoester lubricant of this invention ranges from about 0.15% to about 1.5% by weight. The cationic lubricant is present in an active weight amount of from about 0.01% to about 0.1% by weight. These amounts are based on the weight of a mixture of the active ingredients in water. Other components of the sizing composition may include a coupling agent, a hydrolyzing agent for hydrolysis of the coupling agent and other conventional additives and processing aids.

The compositions are typically formulated by blending the individually premixed ingredients to form a concentrate, then diluting this concentrate to provide an aqueous dispersion. The ingredients such as the film-forming polymer, the coupling agent, the hydrolyzing agent, the lubricants and processing aids are used in amounts effective to formulate a stable aqueous dispersion having a storage stability of up to about 72 hours at temperatures of from about 50° F. to about 120° F., and a pH of from about 3.5 to about 5.0.

Another aspect of this invention is a method of treating the reinforcing fibers comprising the steps of formulating an aqueous sizing composition comprising low concentrations

of a cationic lubricant and a nonionic lubricant; and contacting one or more reinforcing fibers with the sizing composition. The sizing can be applied to fibers as they are attenuated from a bushing apparatus conventionally used in fiber production.

#### DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS OF THE INVENTION

A particularly desirable aspect of the invention is the combination of certain cationic and nonionic lubricants in low concentrations, such that the desired effects of increased resistance to fuzz development, good wetting ability, and at the same time, improved roving package stability, are achieved.

The cationic lubricant useful in the invention is selected from the group consisting of partially amidated long-chain polyalkylene imines. The partially amidated polyalkylene imines usually have a residual amine value of from about 200 to about 800 and are reaction products of a mixture of about  $C_{12}$  to about  $C_{18}$  fatty acids with a polyethylene imine having a molecular weight from about 800 to about 50,000. The amines suitable for forming the fatty acid salt of this reaction product are preferably tertiary amines of substantially low molecular weight, for example with the alkyl groups attached to the nitrogen atom having from about 1 to about 6 carbons. Preferably, the fatty acid moiety of the salt preferably includes from about 12 to about 22 carbon atoms. Most preferably, the partially amidated polyalkylene imine is a condensation reaction product of polyethylene imine with a fatty acid selected from the group consisting of pelargonic and caprylic acids, which for example is commercially available from Henkel Inc. under the trademark EMERY 6760T.

The amount of the cationic lubricant required for successful practice of this invention is an amount sufficient to provide a level of the active lubricant that will form a coating with low fuzz development, while yielding excellent roving package stability. An excessive amount of this ingredient is undesirable because at high levels, poor package build and deformation of the product results. The amount of partially amidated polyalkylene imine cationic lubricant in the size coatings of this invention may therefore preferably vary from about 0.01% to about 0.1% active weight, in an aqueous formulation of the composition. This amount is low enough to provide an effective coating without any of the adverse effects of using a higher concentration. Preferably, the active weight of the cationic lubricant is from about 0.05% to about 0.07% weight.

The nonionic lubricant is a polyoxyalkylated polyalkylene glycol ester, such as a fatty acid monoester. Preferably, the nonionic lubricant of this invention is an alkoxylated polyethylene glycol fatty acid ester. An example of a preferred ester is an ethoxylated polyethylene glycol fatty acid monoester. A particularly preferred nonionic lubricant is a mono-oleate ester having about 400 ethylene oxide groups, marketed commercially as PEG 400 MO by Henkel Chemicals. The concentration of the glycol monoester lubricant in the sizing compositions of the invention ranges from about 0.15% to about 1.5% by weight, with a range of about 0.60% to about 0.81% by weight being preferred. Most preferably, the active weight of nonionic lubricant is about 0.76% weight.

Optimally, a combination of about 0.76% weight of the monoester lubricant and about 0.01% active weight of the cationic lubricant may be used. These amounts are based on the weight of a mixture of the active sizing composition in water.

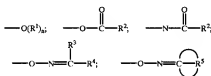
The film-forming polymer component of the composition may be selected from polymers known in the art as useful in

5

film coating of glass and carbon fibers. Some examples of these film-forming polymers include resins such as epoxies, polyamides, polyesters, polyvinyl acetates, styrenated acrylics, phenolics, melamines, nylons, acrylics, PVC, polyolefins, polyurethanes and nitrile rubbers.

Optionally, the sizing composition also includes one or more additives selected from the group consisting of coupling agents, wetting agents and hydrolyzing agents.

The coupling agent preferably used in this invention have hydrolyzable groups that can react with the glass surface to remove unwanted hydroxyl groups; and one or more groups that can react with the film-forming polymer to chemically link the polymer with the glass surface. Preferably, the coupling agent is one that has 1-3 hydrolyzable functional groups that can interact with the surface of the glass fibers, and one or more organic groups that are compatible with the polymer matrix. The preferred coupling agents of this invention include compounds selected from the group consisting of organosilanes. Examples of hydrolyzable groups associated with these organosilanes include vinylic, amino and imino groups such as:



and the monohydroxy and/or cyclic  $\text{C}_2\text{---C}_3$  residue of a 1,2- or 1,3-glycol, wherein  $\text{R}^1$  is H or  $\text{C}_1\text{---C}_4$  alkyl;  $\text{R}^2$  is H or  $\text{C}_1\text{---C}_4$  alkyl;  $\text{R}^3$  and  $\text{R}^4$  are independently selected from H,  $\text{C}_1\text{---C}_4$  alkyl or  $\text{C}_6\text{---C}_8$  aryl; and  $\text{R}^5$  is  $\text{C}_6\text{---C}_8$  alkylene; and n is an integer from 1 to 3. The organosilanes of this invention are preferably those which produce 1-3 hydroxyl groups for bonding at the inorganic glass surface to form  $\text{O---Si---O}$  bonds, and which also possess at least one organic group for binding to the matrix resin. Some examples of the organosilanes defined above include 3-amino-propyldimethylethoxysilane, gamma-aminopropyltriethoxysilane, gamma-aminopropyltrimethoxysilane, beta-aminomethoxytriethoxysilane, N-beta-aminoethylamino-propyltrimethoxysilane, gamma-isocyanatopropyltriethoxysilane, vinyl-trimethoxysilane, vinyl-triethoxysilane, allyl-trimethoxysilane, mercaptopropyltrimethoxysilane, mercaptopropyltriethoxysilane, glycidyloxypropyltrimethoxysilane, 4,5-epoxycyclohexylethyltrimethoxysilane, ureidopropyltrimethoxysilane, ureidopropyltriethoxysilane, chloropropyltrimethoxysilane and chloropropyltriethoxysilane. Mixtures of two or more of these organosilanes may be used.

Particularly preferred organo functional silane coupling agents for the practice of this invention include vinylic silanes, which are useful in unsaturated resins; and amino silanes, which are useful promoters or coupling agents for resins such as epoxies, phenolics, melamines, nylons, acrylics, PVC, polyolefins, polyurethanes and nitrile rubbers. In one preferred embodiment, the organosilane ingredient is a mixture of a methacrylate-silane, most preferably gamma-methacryloxypropyltrimethoxysilane (a vinylic silane also known commercially as A-174); and an amino silane, most preferably gamma-aminopropyltriethoxysilane (A-1100). A-174 and A-1100 are commercially available, for example from Waco Chemical Co.

The wetting agent is added to facilitate contact between the dispersion and the fiber surface. Any conventional wet-

6

ting agent that is compatible with the other ingredients of the sizing composition can be used. In the preferred embodiment, the wetting agent is mono-pentarythritol, at a concentration of about 0.10% to about 0.15% weight.

A hydrolyzing agent may also be included to hydrolyze one or more of the coupling agents. Suitable hydrolyzing agents include hydrochloric, acetic, formic, citric, oxalic and phosphorous acids. Preferably, an effective concentration of acetic acid is used to carry out the hydrolyzing step. For example, about 0.21% weight of acetic acid may often be sufficient.

The sizing compositions of the invention are formulated as a concentrate, with the appropriate poundage per gallon based on the percentage weight of active solids in each ingredient. The ingredients are each premixed in a tank with demineralized water and agitated for the appropriate period of time necessary to achieve a homogeneous dispersion or solution. The premixed ingredients are then fed to a mix tank and agitated. Demineralized water is added as required to provide the desired mix-solids concentration. The mix solids concentration may vary from about 2% to about 12% by weight in the aqueous dispersion. Preferably, the total amount of mix solids is about 6.5% weight, based on the weight of the total dispersion.

The finished mixture typically has a pH of between 3.5 and 5.0. The composition can generally be stored for up to 72 hours at a temperature of between 65-85° F. without deleterious effect.

The aqueous sizing composition can be applied to the reinforcing fibers by any method known to those skilled in the art. In the preferred embodiment, the composition is applied to glass fibers after they have been attenuated from a fiber-forming bushing. Fibers exiting the bushing may be passed through a coating apparatus where the sizing treatment is applied, or the composition may otherwise be contacted with the fibers according to methods familiar to one skilled in the art. For example, the coating may be applied to the surface of the fibers by spraying, dipping, roll-coating, or other coating means known in the art. After the sizing is applied, the fibers may be gathered into strands or rovings and wound to build a forming package.

As one means of building the forming package, glass fibers attenuated from the fiber-forming bushing are combined into one or more strands as they are turned onto or passed through a gathering apparatus. A winder located below the gathering apparatus simultaneously collects the strands onto a rotating collet. The strands are thus formed into a cylindrical forming package. The rate of attenuation of the fibers and the rate of winding can be controlled so as to create a uniformly wound package having a desirable size. The winding operation may also be modified such that more than one forming package can be wound at the same time from the strands attenuating from the bushing. The forming packages can then be used in combination with a desired polymer matrix material to form composites and composited articles.

Glass fiber reinforced polymer matrices are commonly used outdoors or in corrosive environments. Applications for pultruded composites include ladder rails, sucker rods, antennae, railings, conduits, I-beams, H-beams and channel angles. Clear or translucent reinforced plastic panel applications include solar collectors, skylights, artificial light fixture covers, patio covers, and highway signs and markings. The composites may also be used in pigmented reinforced sheet molding compound (SMC) applications, such as satellite dishes, showers, bath tubs, automotive body panels, valve covers, spoilers and bumpers.

#### EXAMPLES

To formulate the composition, each of the ingredients was first premixed in demineralized water maintained at a tem-



7

perature of 75±5° F. The amount of water placed in the premix tank was varied according to the ease of dispersion of the ingredients. The premix was agitated sufficiently to provide a homogeneous solution or dispersion, and then added to the main mix tank. Compatible ingredients were optionally premixed together in a master batch before being added to the main tank. The mixed ingredients were agitated together in the main mix tank for about 5 minutes, after which the mix solids were checked. Demineralized water was added to the concentrate formed in order to adjust the level of mix solids to a level that would provide the targeted level of strand solids. This level was typically from 5.5% to 6.9% by weight, based on the weight of the dispersion.

The following exemplary formulations are representative of the invention:

Example 1

Material	% Active solids <sup>(1)</sup>	% by weight as received	Lb./100		% Active Concentration <sup>(6)</sup>
			gallons as received <sup>(2)</sup>	Kg/100 liters as received <sup>(3)</sup>	
FFP	56	7.01	58.37	6.995	3.906
A-174	68	0.97	8.10	0.97	0.658
A-1100	58	0.24	2.02	0.242	0.140
Acetic Acid <sup>(4)</sup>	100	0.21	1.72	0.206	0.206
PEG 400 MO	100	0.64	5.37	0.643	0.642
EMERY 6760T	12.5	0.20	1.67	0.200	0.050
Mono FE <sup>(5)</sup>	100	0.10	0.87	0.305	0.104
DM Water	0	90.62	754.88	90.466	—

<sup>(1)</sup>Percentage weight solids used to calculate the predicted size mix solids.

<sup>(2)</sup>Master premix is allowed for acetic acid, Emery 6760 and Mono FE.

<sup>(3)</sup>As received, mix solids are calculated at 5.50%.

<sup>(4)</sup>Concentration of active species in the sizing composition.

FFP - film-forming polymer emulsion, for example an emulsion of DOW-337, Dow Chemical Inc.

A-174 - gamma-methacryloxypropyltrimethoxysilane, Witco Chemical Co.

A-1100 - preferably gamma-aminopropyltriethoxysilane, Witco Chemical Co.

Example 1

Material	% Active solids <sup>(1)</sup>	% by weight as received	Lb./100		% Active Concentration <sup>(6)</sup>
			gallons as received <sup>(2)</sup>	Kg/100 liters as received <sup>(3)</sup>	
FFP	56	6.98	58.11	6.964	3.924
A-174	68	0.97	8.06	0.966	0.661
A-1100	58	0.24	2.01	0.241	0.141
Acetic Acid <sup>(4)</sup>	100	0.21	1.71	0.205	0.206
PEG 400 MO	100	0.64	5.35	0.641	0.645
EMERY 6760T	12.5	0.40	3.33	0.399	0.025
Mono FE <sup>(5)</sup>	100	0.10	0.87	0.104	0.105
DM Water	0	90.46	753.57	90.309	—

It is believed that Applicant's invention includes many other embodiments which are not herein specifically described, accordingly this disclosure should not be read as being limited to the foregoing examples or preferred embodiments.

I claim:

1. A sizing composition for coating fibers comprising from 0.01 to about 0.1 percent weight of a cationic lubricant wherein the cationic lubricant is a partially amidated polyalkylene imine and from about 0.15 to about 1.5 percent weight of a nonionic lubricant wherein the nonionic lubricant is a polyoxyalkylated polyalkylene glycol ester.

8

2. The composition of claim 1, wherein the nonionic lubricant is ethoxylated polyethylene glycol mono-oleate.

3. The composition of claim 1 wherein the amidated polyalkylene imine cationic compound is a condensation product of polyethylene imine with a fatty acid selected from the group consisting of pelargonic and caprylic acids.

4. The composition of claim 1, further comprising a coupling agent.

5. The composition of claim 4, wherein the coupling agent comprises one or more compounds selected from the group consisting of vinyl silanes, amino silanes and mixtures thereof.

6. The composition of claim 5, wherein the vinyl silane coupling agent is selected from the group consisting of acrylate- and methacrylate-substituted silanes.

55

7. The composition of claim 6, wherein the vinyl silane coupling agent is gamma-methacryloxypropyltriethoxysilane.

8. The composition of claim 5, wherein the amino silane coupling agent is gamma-aminopropyltriethoxysilane.

9. The composition of claim 8, wherein the coupling agent is a mixture of gamma-methacryloxypropyltriethoxysilane and gamma-aminopropyltriethoxysilane.

10. The composition of claim 1, further comprising a wetting agent.

60

65

11. The composition of claim 10, wherein the wetting agent is mono-pentaerythritol.

12. The composition of claim 10 further comprising a hydrolyzing agent for hydrolyzing the coupling agent.

13. The composition of claim 12, wherein the hydrolyzing agent is acetic acid.

14. A sizing composition for coating fibers comprising:

- a) from about 0.64 to about 0.81 percent weight of nonionic lubricant which is an ethoxylated polyethyl-ene glycol mono-oleate;

b) from about 0.050 to about 0.063 percent weight of a cationic lubricant which is a partially amidated poly-alkylene imine compound;

c) from about 0.65 to about 0.83 percent weight of a methacrylate-based organosilane coupling agent; and

d) from about 3.9 to about 4.1 percent weight of an emulsion of an epoxy film-forming polymer.

\* \* \* \* \*

Exhibit C



US006432482B1

**(12) United States Patent**  
**Jaffee et al.****(10) Patent No.: US 6,432,482 B1**  
**(45) Date of Patent: Aug. 13, 2002****(54) METHOD OF MAKING A MULTIPLE LAYER  
NONWOVEN MAT**5,102,728 A 4/1992 Gay et al. .... 428/268  
5,112,678 A • 5/1992 Gay et al. .... 428/268**(75) Inventors:** Alan Michael Jaffee, Bowling Green;  
Richard Emil Kajander, Toledo, both  
of OH (US)

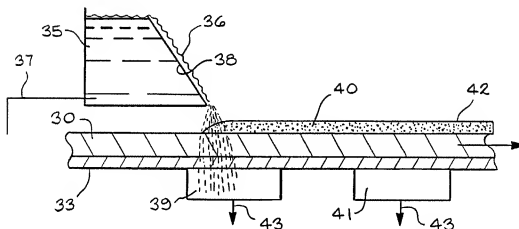
\* cited by examiner

**(73) Assignee:** Johns Manville International, Inc.,  
Denver, CO (US)*Primary Examiner*—Michael Barr  
*Assistant Examiner*—Rebecca A Blanton  
(74) *Attorney, Agent, or Firm*—Robert D. Touselec**(\*) Notice:** Subject to any disclaimer, the term of this  
patent is extended or adjusted under 35  
U.S.C. 154(b) by 0 days.**(21) Appl. No.: 09/665,735****(22) Filed: Sep. 20, 2000****Related U.S. Application Data****(62)** Division of application No. 09/224,391, filed on Dec. 31,  
1998, now Pat. No. 6,187,697.**(51) Int. Cl.<sup>7</sup> .....** B05D 3/02**(52) U.S. Cl. ....** 427/385.5; 427/389.7;  
427/389.8; 427/389.9; 427/393.6**(58) Field of Search ....** 427/385.5, 186,  
427/201, 372.2, 389.7, 389.8, 389.9, 393.6,  
420, 421**(56) References Cited****U.S. PATENT DOCUMENTS**

5,001,005 A • 3/1991 Blaupied ..... 428/283

**(57) ABSTRACT**

The invention includes fibrous nonwoven multiple layer mats having at least two layers with a body portion layer and a surface portion layer having fine fibers and/or particles therein, both layers being bonded together and to each other with a same resin binder. Preferably most or essentially all of the particles and/or fibers in the surface layer are larger than openings between the fibers in the body portion of the mat. The mats produced according to this invention are useful as a facer for all types of boards such as wood boards, wood product boards, insulating boards and hard boards of all types, and also as reinforcement and dimensional stabilizers for making a large number of novel laminate products and for a myriad of other uses. These mats are made on a wet laid nonwoven mat machine with a modification to the binder preparation system, an inventive step in the preparation of the binder and in the selection of ingredients for a binder slurry.

**8 Claims, 2 Drawing Sheets**

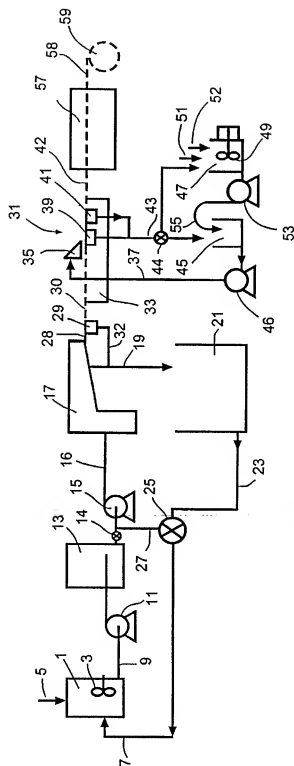


FIG. 1

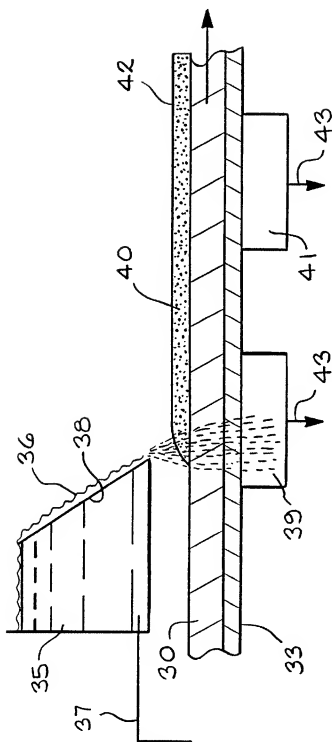


FIG. 2

# METHOD OF MAKING A MULTIPLE LAYER NONWOVEN MAT

This application is a division of Ser. No. 09/224,391 filed Dec. 31, 1998 now U.S. Pat. No. 6,187,697.

The present invention involves fibrous nonwoven mats having at least two layers with a surface layer having fine fibers and/or particles therein, both layers being well bonded together and to each other with a same resin binder. The mats produced according to this invention are useful as a facer for all types of boards such as wood boards, wood product boards, insulating boards and hard boards of all types, and also as reinforcement and dimensional stabilizers for making a large number of laminate products and for a myriad of other uses. These mats are made on a conventional wet laid nonwoven mat machine except for a modification to the binder preparation system, an inventive step in the preparation of the binder and in the selection of ingredients for a binder slurry.

It is known to make nonwoven fibrous mats from fibers, such as glass, polyester, polypropylene, polyethylene, cellulose, ceramic and many other types of fibers, and to bond these fibers together into mats with a thermosetting or thermoplastic resin binder, like urea formaldehyde, acrylic, melamine formaldehyde with or without urea additions, polyvinyl acetate and other resins, or mixtures thereof to make fibrous nonwoven mats. Such mats are used to make a myriad of roofing, building and automotive products. It is also known to use an acrylic copolymer latex, such as a self-cross linking acrylic copolymer of an anionic emulsifying type as one component of at least a two component binder for bonding glass fibers and particulate thermoplastic to make a glass fiber reinforced sheet that can later be hot molded into various shapes and articles, as disclosed in U.S. Pat. No. 5,393,379. It is also known to face gypsum board with fibrous nonwoven mats as disclosed in U.S. Pat. Nos. 5,772,846 and 4,647,496.

It is also known to add particles of thermoplastic resin to an aqueous fiber slurry used to make a mat that can later be hot stamped or thermoformed. When this is done, the resulting nonwoven mat is uniform throughout its thickness. Examples of nonwoven fiber glass mat containing particles of thermoplastic like polyvinyl chloride, polypropylene, etc. are disclosed in published European Patent Applications 0148760 and 0148761. In EP 0148760 the mat is bound together with aqueous binders like polyvinyl alcohol, starch, phenol formaldehyde, etc. According to the disclosures of both these EP applications the particulate thermoplastic component(s) is present in the mat in amounts of 40-80 percent by weight, and the mat is subjected to elevated temperature and pressure to fuse and consolidate the thermoplastic particles into a continuous thermoplastic matrix reinforced with glass fibers. Such mats would not be suitable as a facer for the insulating gypsum board product, such as the board disclosed in U.S. Pat. No. 4,647,496.

One surface of fibrous nonwoven mats made on a wet laid mat machine having no coating equipment thereon usually differs slightly from the opposite surface due to binder migration and/or one side laying on a wire belt while the other side is fully exposed and not in physical contact with any confining article during forming and drying. Nevertheless, the two sides are fairly similar in permeability and smoothness and both sides have fibers exposed. It is known to coat a mat on-line after drying and to spray very light or very thin coating compositions on a wet mat before drying. These coating methods either require extra equipment and mat handling or are inadequate for heavier coat-

ings unless the forming speed is slowed down to unacceptable levels or for coatings containing particles over certain sizes. It is also known to coat a nonwoven mat, usually in a secondary operation, to seal one surface of the mat and/or to produce a smoother surface.

It would be desirable to make a mat having a smooth and less permeable surface at normal mat forming speeds without having to add equipment to the machine above the formed mat where it gets dirty and is difficult to clean without getting foreign material into the mat being produced and without adding substantial additional processing operations to the nonwoven mat processes and lines. While gypsum board faced with fiber glass mats has performed well in the past, it is desirable to hide the glass fibers better to prevent the fibers at the surface of the mat from partly or entirely breaking loose and from presenting a rough surface; but this has not been accomplished to the degree desired prior to this invention.

## SUMMARY OF THE INVENTION

The present invention includes a multiple layer fibrous nonwoven mat having a body portion, the body portion comprising a mass of nonwoven fibers, with or without particles, bonded together with a resin binder, and a surface portion containing fibers and/or particles bonded together with the same said resin binder, the surface portion being substantially different than the major or body portion of the nonwoven mat. The body portion makes up a major portion of the basis weight (weight per unit area) of the mat while the surface portion makes up a minor portion of the basis weight of the mat. The fibers used for the surface portion are preferably shorter than one-quarter inch and longer than 100 microns.

Particles, when used in the surface portion according to this invention, are preferably sized so that less than a few percent, preferably less than one wt. percent of the particles will pass through the openings between the fibers in the nonwoven mat. The smaller the diameter of the fibers in the body portion the smaller the openings in the body portion and the smaller the particles and fibers that can be used in the surface portion. Preferably, the particles are within the size range of minus 40 and plus 100 U.S. standard mesh and can be of a lower bulk density than water. If the particles are too small, too many will flow part way or all the way through the body portion of the mat which is less desirable. It is permissible for some or a small portion of particles to flow into at least an interface portion of the body portion of the mat. This latter embodiment produces a better bond between the two layers, the body portion and the surface portion, and also helps to reduce the permeability of the layered mats. The surface portion of the mat of the present invention has a substantially lower permeability or pore size, or both, than the body or major portion of the fibrous nonwoven mat. An exposed surface of the surface portion can also be substantially smoother than an exposed surface of the body portion of the fibrous nonwoven mat. Preferably, at least 99 percent of the particles or fibers in the binder put onto the mat end up in the surface portion layer of the multiple layer nonwoven mat. Preferably the multiple layer mats of the present invention have two layers, a body portion layer and a surface layer portion.

The invention also includes a method of making the fibrous nonwoven mat described above comprising dispersing fibers, such as glass fibers, in an aqueous slurry, collecting the dispersed fibers onto a moving permeable support to form a fibrous nonwoven layer, removing excess water from the fibrous nonwoven layer, applying an aqueous resin

3

latex binder containing particles and/or fibers to the top surface of the rapidly moving wet nonwoven fibrous layer, removing excess latex or aqueous resin, drying the nonwoven mat and curing the resin binder to form a nonwoven mat having a surface layer that differs substantially from the fibrous nonwoven body of the mat. The aqueous resin binder can also be foamed before using.

#### DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic of a conventional wet mat process having an optional binder mixing tank, according to the present invention.

FIG. 2 is a schematic cross section of a portion of the process of FIG. 1 showing the binder application portion and the practice of the present invention to make mats of the present invention.

#### DETAILED DESCRIPTION OF THE INVENTION

It is known to make reinforcing nonwoven mats from glass fibers and to use these mats as substrates in the manufacture of a large number of roofing and other products. Any known method of making nonwoven mats can be used in this invention, such as the conventional wet laid processes described in U.S. Pat. Nos. 4,129,674, 4,112,174, 4,681,802, 4,810,576, and 5,484,653, the disclosures of each being hereby incorporated herein by reference. In these processes a slurry of glass fiber is made by adding glass fiber to a typical white water in a pulper to disperse the fiber in the white water and to form a slurry having a fiber concentration of about 0.2-1.0 weight %, metering the slurry into a flow of white water to dilute the fiber concentration to 0.1 wt. percent or less, and continuously depositing this mixture onto a moving screen forming wire to dewater and form a wet nonwoven fibrous mat. This wet nonwoven mat is then conveyed through a binder application where an aqueous resinous binder is applied in excess, the surplus is removed by suction and the wet, bindered mat is then dried and the binder cured to form a nonwoven mat product.

The method of the present invention comprises a modification to the binder preparation portion of otherwise conventional mat making processes. Most nonwoven mat processes and forming machines are suitable for modification and use with the present invention, but preferred are the wet laid nonwoven mat processes and machines wherein an aqueous slurry containing fibers is directed onto a moving permeable screen or belt called a forming wire to form a continuous nonwoven wet fibrous mat.

FIG. 1 is a schematic of a preferred wet laid system for practicing the invention. Fibers 5 are fed continuously at a controlled rate into a pulper 1 along with a conventional whitewater through a pipe 7, also continuously and at a controlled rate. An agitator 3 in the pulper 1 mixes and disperses the fibers in the whitewater. The resultant concentrated fibrous slurry flows continuously through a pipe 9 into an optional pump 11 which pumps the concentrated slurry into a fiber slurry holding tank 13. The concentrated fiber slurry is preferably metered continuously from the holding tank 11 with a valve 14 and into a metered flow of deaired whitewater 27 to form a diluted fibrous slurry. The valve 25 meters a correct rate of deaired whitewater to the pulper 1 via pipe 7 and a correct rate of deaired whitewater 27 to form the diluted fiber slurry. The diluted fibrous slurry flows into pump 15 and is pumped to the mat forming machine 17, which can be of any width and typically is wide enough to make a finished mat 12 feet wide or wider. Alternative

4

forming methods for making the body portion of the nonwoven mat include the use of well known paper or board making processes such as cylinder forming, dry forming or air laid, etc.

The preferred processes for the production of mats of the present invention are those known processes using mat forming machines 17 like a Hydroformer™ manufactured by Voith—Sulzer of Appleton, Wis., or a Deltaformer™ manufactured by North County Engineers of Glens Falls, N.Y. In these machines, the diluted fiber slurry flows horizontally against an inclined moving permeable belt or forming wire (not shown) where the fiber is collected and builds up in a random pattern to form a wet mat 28 while the whitewater passes through the forming wire becoming somewhat foamy (due to contained air) and is transported to a dewatering tank 21 via pipe 19. The wet mat is dewatered to the desired level with a suction box 29, and the foamy whitewater removed is piped through pipe 32 to the dewatering tank 21, preferably via the pipe 19.

This wet nonwoven layer of fiber 30, the body portion, is then preferably, but not necessarily, transferred to a second moving screen 33 and run through a binder application saturating station 31 where an aqueous binder is applied to the mat in any one of several known ways. According to the method of the invention this aqueous binder will also contain a significant amount of particles and/or fibers that are larger than pores or openings between the fibers in the wet nonwoven mat. A binder slurry is pumped at a controlled rate from a binder slurry holding tank 45 via a controlled rate pump 46 such that more binder than is needed is fed through a pipe 37 to a binder applicator 35 where the binder slurry is applied in excess to the wet mat body portion 30.

The binder slurry is prepared by feeding an aqueous resin binder 52 at a desired rate and fibers, particles or both 51 to a binder mix tank 47 having an agitator 49 therein to disperse the fibers, particles or both 51 in the aqueous binder 52. The binder slurry is then pumped to the binder holding tank 45 with a metering pump 53 and pipe 55. The metering pump 53 speeds up and slows down with the speed of the mat line or windup 59. The metering pump 53 is also controlled to provide the desired thickness of the surface portion of the two layered mat. The resin content in the binder slurry and the degree of vacuum in the suction boxes 39 and 41 are varied to control the binder resin content of the body portion and the surface portion of the two layered mat. The binder slurry can be prepared continuously or in batches as is well known. When prepared continuously, all ingredients of the slurry are carefully metered in known ways to insure that the desired composition of the finished mat is maintained.

When the aqueous binder slurry is applied to the wet nonwoven mat or body portion 30, the particles and/or fibers therein will build up a surface portion 40 (FIG. 2) on the binder application side of the wet nonwoven body portion 30 while the aqueous resin binder portion of the binder slurry will saturate both the surface portion 40 and the body portion 30, the original wet nonwoven fibrous layer, of the resulting wet nonwoven mat. Preferably, excess aqueous binder slurry is applied using a curtain coater, such as supplied by North County Engineers of Glens Falls, N.Y., but other known methods of application and equipment that will handle the particles and/or fibers in the binder and that will apply this at the rate required to the top of the wet body portion of the mat will work. As shown in FIG. 2, the binder slurry flows over a lip of an inclined surface 38 of a curtain coater type of binder applicator 35 and onto the body portion 30 building up a surface portion 40 of fibers and/or particles 52



5

that were in the binder slurry. As shown, the aqueous binder portion also flows into the body portion 30 also coating the fibers in the body portion 30 and the excess aqueous binder portion flows out of the body portion 30, through the permeable belt 33 and into a first suction box 39. The binder saturated mat is then run over one or more suction boxes 41 while still on the moving permeable belt 33 to remove excess binder and water which is returned to the binder mix tank 47, and/or to the binder holding tank 45, via pipe 43.

The wet, banded nonwoven mat 42 is then transferred to a moving conventional permeable, oven belt (not shown) and run through an oven 57 to dry the wet mat 42 and to cure (polymerize) the polymeric based resin binder which bonds the fibers, and particles when particles are present in the surface portion, together forming the finished inventive mat 58 which can be wound into a roll 59 using conventional mat winding equipment. When the fibers and/or particles in the surface portion are of an organic thermoplastic or a flowable thermoset, it is often desirable to heat the dry mat to a temperature that will fuse and flow the fibers and/or particles together into a layer having a relatively smooth surface.

The body portion of the mats of the present invention preferably contain about 80-99.5 wt. percent of the total weight of fibers, and particles when particles are present, in the dry, finished nonwoven mat with the particles and/or, fibers in the surface portion of the mat being about 0.5-20 wt. percent of the fibers and particles in the dry, finished nonwoven mat. The resin binder content of the mat can vary greatly, but usually is about 5-35 wt. percent of the nonwoven mat.

Preferably, the majority of the fibers are glass fibers and most preferably all the fibers are glass fibers, but this invention is equally applicable to ceramic, natural and polymer fiber nonweaves and to nonweaves made from mixtures of any combination of these types of fibers. The fibers used in the nonwoven body portion should be at least 0.25 inch long or longer, more preferably at least one-half inch or three-quarters inch long and most preferably at least about one inch long, but mixtures of fibers of different lengths and/or fiber diameters can be used as is known. It is preferred that these fibers be coated with a silane containing size composition as is well known in the industry.

The glass fibers can be E, C, T, S or any known type glass fiber of good strength and durability in the presence of moisture and mixtures of lengths and diameters. The preferred fibers are K or M 137 and K or M 117 E glass fibers available from Johns Manville International, Inc. of Denver, Colo., but most any commercially wet chop glass fiber product will be suitable. While the majority of the fibers are glass fibers in the preferred body portion, a minor portion of non-glass fibers can also be included, such as man made or natural organic fibers like Nylons™, polyester, polyethylene, polypropylene, cellulose or cellulose derivatives, etc.

The binder used to bond the fibers together can be any binder capable of bonding the fibers together. A wide variety of binders are used to make nonweaves with urea formaldehyde (UF), melamine formaldehyde (MF), polyester, acrylics polyvinyl acetate, UF and MF binders modified with polyvinyl acetate and/or acrylic are typically used.

After the binder is applied and adjusted to the desired level with one or more suction boxes, the wet, banded mat is transferred on an oven belt or wire and the mat is dried and the binder is cured to form the finished mat. The mat is heated to temperatures of up to about 500 degrees F. in the oven, depending on the type of binder used and/or the nature of the particles and/or fibers in the surface portion.

6

The particles and/or fibers used to make the surface portion of the two layered mat should not be soluble in the aqueous resin binder slurry, but could be slightly soluble. Otherwise, the particles and fibers can be of almost any material. Some examples of suitable materials are plastic particles like phenol formaldehyde, regular or modified polyethylene and polypropylene, nylon, polyvinyl alcohol, glass beads or microspheres, expanded clay, mica, flake glass, raw or expanded vermiculite, raw or expanded perlite, clay, organic or inorganic powders, microfibers, mineral wool, and the like.

One preferred mat has a basis weight target of 1.8 pounds per 100 square feet and contains ¼ inch long 13 micron glass fibers bonded together with a known modified urea formaldehyde (UF) resin binder. In the body portion and ¼ inch long 3 denier cellulose acetate fibers bonded together with the same UF resin binder in a surface portion on one side of the preferred mat. The composition targets for the mats of this preferred embodiment are about 75 wt. percent of glass fibers, 20-22.5 wt. percent of UF resin binder and 2.5-5 wt. percent of cellulose acetate fibers.

#### EXAMPLE 1

A fiber slurry was prepared in a well known manner by adding three-quarter inch long E glass type H 117 wet chop glass fiber from Johns Manville International, Inc. having a silane containing chemical sizing on the surface, as is well known, to a known cationic white water containing Natrosol™ thickening agent available from Aqualon, Inc. of Wilmington, Del., and a cationic surfactant C-61, an ethoxylated tallow amine available from Cytec Industries, Inc. of Morristown, N.J., as a dispersing agent to form a fiber concentration of about 0.8 weight percent. After allowing the slurry to agitate for about 5 minutes to thoroughly disperse the fibers, the slurry was metered into a moving stream of the same whitewater to dilute the fiber concentration to a concentration averaging about 0.05 to 0.06 weight percent before pumping the diluted slurry to a headbox of a pilot scale model of a North Hydroformer™ where a wet nonwoven mat was continuously formed.

The wet mat was removed from the forming wire and transferred to a curtain coater binder applicator where an aqueous binder slurry was applied to the mat. This binder slurry was made by mixing a plus 100 mesh Novolac™, a phenolic resin powder, available from Georgia Pacific Corporation, Atlanta, Ga., with an aqueous modified UF resin. The modified resin was made by adding about 7.5 wt. percent, based on the UF solids, of Duraset™ 827, available from Franklin International of Columbus, Ohio, and about 5 wt. percent of hexamethylene tetramine as a cross linking agent to a Georgia Pacific 2928 UF resin latex containing 54-56 wt. percent solids. The amount of Novolac™ powder in the aqueous UF binder slurry was sufficient to produce a mat having a surface portion containing about 15 wt. percent Novolac™ particles, based on the weight of fiber in the body portion of the mat.

The wet mat was then transferred to an oven belt and carried through an oven to dry the mat and to heat the mat to a temperature of about 350-400 degrees F. for about several seconds to cure the resin binder and to fuse and cure the Novolac™ particles. The Novolac™ particles also flowed to form a coating layer on the body portion of the two layered mat. The basis weight of the mat produced was about 1.83 lbs./100 sq. ft. The resultant two layered mat had the following properties:

Thickness	30 mils
Loss On Ignition	33.4 weight percent
Machine Direction Tensile	120 lbs./3 inch width
Cross Machine Tensile	136 lbs./3 inch width
Air Permeability	565 cu.ft./min./sq.ft.

The air permeability of this mat compares with an air perm of more than 700 on a conventional fiber glass non-woven mat of this basis weight. The bonded Novolac™ surface portion of the mat of this example is much smoother than the opposite side of the mat; and substantially fewer of the glass fibers of the body portion are visible on the surface of the surface portion. This mat, when bonded to gypsum board such that the body portion is next to the gypsum board and the surface portion of the mat is exposed, is expected to perform functionally as well as the conventional fiber glass mats normally used on gypsum board. In addition, gypsum board faced with the mat of this example should have a more friendly feel and not cause an itching issue with the people handling and installing the faced gypsum board, which is a substantial improvement.

Similar results can be achieved with different amounts of surface layer such as when the phenolic resin powder in the surface layer ranges from about 5 to about 20 weight percent of the fiber in the body portion. Other types of phenolic resin can be used. Other types of aqueous resinous binder can also be used, especially when the mat is to be used for other applications.

#### EXAMPLE 2

Another mat was made in exactly the same way as in Example 1, except that three-quarter inch long K 117 fiber from Johns Manville International, Inc. was used for the body portion. The binder slurry for the mat contained one-quarter inch long 3 denier cellulose triacetate fiber (enough to produce a cellulose triacetate content, essentially all in the surface portion, in the two layered mat of about 15 wt. percent, based on the weight of glass fiber in the body portion) and the curing temperature was about 400 degrees F. The basis weight of the mat was 1.92 lbs. per 100 square feet. The other properties were as follows:

Thickness	35 mils
Loss On Ignition	31 weight percent
Machine Direction Tensile	99 lbs./3 inch width
Cross Machine Tensile	119 lbs./3 inch width
MD + CD Tear Strength (Elmendorf)	455 grains

This mat can be used as a facer for fiber glass insulation and for board products with the glass fiber base portion bonded to the insulation or board product and the surface portion of bound cellulose acetate fibers exposed.

#### EXAMPLES 3-8

Fire resistant mats, and mats having a lowered permeability, are made by using a more refractory material for the surface portion. In this example the procedure was similar to that used in Example 1 except that the binder was aqueous acrylic resins, and mica flakes of different average particle size were added to this aqueous binder in different concentrations to form binder slurries that produced two layer mats of differing thicknesses of the surface portion

which produced mats having different permeabilities. First, a control mat having a basis weight of about 1.55 lbs. per 100 sq. ft. (7.04 grams/sq. ft.) was made by dispersing 0.5 inch long H 117 glass fibers having a diameter of 10 microns in the whitewater and using an aqueous acrylic resin binder to saturate the mat. Enough acrylic resin binder remained in the wet mat to produce an LOI in the dried and cured mat of about 25 wt. percent. The aqueous acrylic resin binder contained B. F. Goodrich's 26138 aqueous acrylic resin and a cross linking agent such as about 5-25 wt. percent of urea formaldehyde or melamine formaldehyde and diluted with whitewater to a solids content of about 25 wt. percent using whitewater from the wet mat machine used to form the base portion of the mat.

After forming a single layer base mat control sample, F120 mica flakes having a median particle size of 405 microns was added to the binder to form a slurry of increasing mica concentration to form two layer mats having various thicknesses of the surface layer portion and consequently increasing basis weights, and various permeabilities as follows:

Mat Description	Basis Wt.	Air Perm. (CFM/Sq.Ft.)
Control - one layer	7.04 g/sq.ft.	580
3-First two layer mat	7.27 g/sq.ft.	560
4-Second two layer mat	7.64 g/sq.ft.	540
5-Third two layer mat	9.10 g/sq.ft.	450

Repeating the above procedure, but substituting V115 mica flakes having a median particle size of 550 microns produced the following mats and mat properties:

Mat Description	Basis Wt.	Air Perm. (CFM/Sq.Ft.)
Control - one layer	7.04 g/sq.ft.	580
6-First two layer mat	7.87 g/sq.ft.	580
7-Second two layer mat	11.59 g/sq.ft.	390
8-Third two layer mat	18.71 g/sq.ft.	320

#### EXAMPLES 9-11

Repeating the above procedure, but changing the acrylic resin to B.F. Goodrich's V-29 acrylic resin while keeping the same type of cross linking agent, using much finer mica flakes (C1000) having a median particle size of 26 microns, and using a combination of 86 wt. percent 0.75 inch long K117 glass fibers having an average fiber diameter of 13 microns and 14 wt. percent of code 206 TEMPSTRAN™ glass microfiber, available from Johns Manville International, Inc., produced the following mats and properties.

\* Code 206 TEMPSTRAN™ is a glass microfiber having an average fiber diameter of between 2 and 3 microns.

Mat Description	Basis Wt.	Air Perm. (CFM/Sq.Ft.)
Control - one layer	6.64 g/sq.ft.	300
9-First two layer mat	8.2 g/sq.ft.	90
10-Second two layer mat	8.8 g/sq.ft.	70
11-Third two layer mat	9.4 g/sq.ft.	30

#### EXAMPLES 12 and 13

These examples were similar to Examples 3-8 except that a mixture of 87 wt. percent of Johns Manville's 0.5 inch

K117 wet chop glass fiber having an average fiber diameter of 13 microns and 13 wt. percent of Johns Manville's Code 206 TEMPESTRAN™ microfibers was used to make the control mat and the base portion of the two layered mats. Another difference was that enough of the aqueous acrylic binder was left in the mat to produce an LOI of about 35 wt. percent. A 1000 K mica, flake product having a median particle size of 81 microns was added to the binder in different concentrations to make different two layered mats. In these examples the basis weight of the mats was kept to 8+/-0.25 by reducing the weight of the glass fibers and binder in the base portion of the mat in an amount similar to the basis wt. of the mica flakes and the binder in the surface portion of the two layered mat.

Mat Description	Basis Wt.	Air Perm. (CFM/Sq.Ft.)
Control - one layer	8.26 g/sq.ft.	140
12-First two layer mat	7.73 g/sq.ft.	120
13-Second two layer mat	8.13 g/sq.ft.	77

Examples 3-13 show that this invention can be used to reduce the permeability of nonwoven mats substantially, and below prior art levels, and with a fire resistant material producing a fire resistant mat of two or more layers in a novel, convenient and economical manner. Many other combinations of materials and two-layered products, or products containing two-layered mats, made using this novel method suggest themselves to the skilled artisan. By using a B stageable aqueous resin binder such as aqueous melamine formaldehyde, phenol formaldehyde or furfuryl alcohol formaldehyde binders instead of the acrylic or other resins mentioned above, and B staging the mat during initial curing, the resultant two layered mats can later be molded hot to make a three dimensional shape and to finish the cure of the resin binder. With sufficient hot molding pressure, the permeability of the mat will be reduced substantially further than that of the mats of Examples 3-13.

The two layered mats can be bonded to a combustible material, like a wood product such as hardboard, particle board, chip board, oriented strand board or plywood with any known adhesive fire resistant adhesive with the body portion of the mat against the combustible material and the mica surface portion exposed by hot pressing at a suitable temperature to fully cure the binder or the adhesive and a pressure sufficient to form the two-layered mat into the desired shape of the mat. This two layered mat facing will increase the time it takes for a fire to burn through the combustible material substantially and allow less expensive materials to pass the fire code tests where they wouldn't pass otherwise. The two layered mats of the present invention can also serve as facers for insulation materials such as fiber glass, mineral wool, ceramic wool, etc. and will also increase the fire resistance and strength of those materials, particularly fiber glass insulation.

Instead of mica flakes, raw or exfoliated vermiculite particles, raw or expanded perlite particles, refractory microballoons, raw or expanded clay, and other refractory powders can be used to make fire resistant mat facers. Also, melamine formaldehyde resin binder can be used instead of the furfuryl alcohol formaldehyde resin. An abrasive facing can be made by using abrasive particles or fibers to form the surface portion.

While the preferred embodiments of the invention have been disclosed in detail, other embodiments within the

described invention and having other functional additives known or obvious to those skilled in the art are considered to be part of the present invention and are intended to be included in the invention claimed below.

What is claimed is:

1. A method of making a multiple layer mat having a fibrous body portion and a surface portion, said body portion containing fibers and said surface portion containing fibers and/or particles, the body portion constituting a major portion of the mat, the body portion and the surface portion being bonded together with the same resinous binder, the method comprising:

- a) forming the body portion by building up fibers in a random orientation to the desired thickness,
  - b) applying a resinous binder slurry to a top surface of the body portion, the binder slurry containing fibers and/or particles such that the fibers and/or particles in the binder slurry build up a surface layer on the top of the body portion while the resinous binder flows through the body portion, the binder content of the mat being between 5 and 35 wt. percent of the multiple layer mat, the resinous binder having been applied as an aqueous slurry wherein the fibers and/or particles in the surface portion were applied as part of the binder slurry, the amount of fibers and/or particles in the surface portion being about 0.5-20 wt. percent of the fibers in the body portion of the mat and wherein the fibers and/or particles in the slurry and in the surface portion are large enough that more than 99 percent of these particles and/or fibers are larger than the openings between the fibers in the body portion, and
  - c) drying and heating the mat to cure the resinous binder in the body portion and in the surface portion.
2. The method of claim 1 wherein at least some of the particles in the binder slurry are smaller than some openings between the fibers in the fibrous base portion of the mat.
3. The method of claim 1 wherein the slurry contains fibers of one-quarter inch length or shorter, but longer than about 100 microns.
4. The method of claim 3 wherein most or essentially all of the particles in the binder slurry are larger than most of the openings between the fibers in the fibrous base portion of the mat.
5. The method of claim 1 wherein the fibers and/or particles in the binder slurry are selected from a group consisting of phenol formaldehyde, regular or modified polyethylene and polypropylene, nylon, polyvinyl alcohol, hot melt and reactive hot melts, glass beads, flakes or microspheres, expanded clay, mica flakes, abrasive particles, diatomaceous earth, raw or expanded vermiculite, raw or expanded perlite, clay, organic or inorganic powders, microballoons, microfibers, mineral wool and expanded clay aggregate.
6. The method of claim 2 wherein the fibers and/or particles in the binder slurry are selected from a group consisting of phenol formaldehyde, regular or modified polyethylene and polypropylene, nylon, polyvinyl alcohol, hot melt and reactive hot melts, glass beads, flakes or microspheres, expanded clay, mica flakes, abrasive particles, diatomaceous earth, raw or expanded vermiculite, raw or expanded perlite, clay, organic or inorganic powders, microballoons, microfibers, mineral wool and expanded clay aggregate.
7. The method of claim 3 wherein the fibers and/or particles in the binder slurry are selected from a group consisting of phenol formaldehyde, regular or modified polyethylene and polypropylene, nylon, polyvinyl alcohol,

## 11

hot melt and reactive hot melts, glass beads, flakes or microspheres, expanded clay, mica flakes, abrasive particles, diatomaceous earth, raw or expanded vermiculite, raw or expanded perlite, clay, organic or inorganic powders, microballoons, microfibers, mineral wool and expanded clay aggregate.

8. The method of claim 4 wherein the fibers and/or particles in the binder slurry are selected from a group consisting of phenol formaldehyde, regular or modified

## 12

polyethylene and polypropylene, nylon, polyvinyl alcohol, hot melt and reactive hot melts, glass beads, flakes or microspheres, expanded clay, mica flakes, abrasive particles, diatomaceous earth, raw or expanded vermiculite, raw or expanded perlite, clay, organic or inorganic powders, microballoons, microfibers, mineral wool and expanded clay aggregate.

\* \* \* \* \*

(x) RELATED PROCEEDINGS APPENDIX

NONE.

CONCLUSION

For all the above reasons, appellants submit that the appealed claims are patentable and respectfully request reconsideration and reversal of the rejection of the final Office Action in view of the above arguments.

The Director is hereby authorized to charge the appropriate fees in connection with this filing to our Deposit Account No. 03-1250, Reference No. FDN-2821, Customer No. 43,309.

Respectfully submitted,

Date: November 14, 2007

/Aasheesh Shravah/

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